

(2)

1 474 891

## PATENT SPECIFICATION

(11) 1 474 891

(21) Application No. 12832/75 (22) Filed 27 March 1975

(44) Complete Specification published 25 May 1977

(51) INT CL<sup>2</sup> A23L 1/04

(52) Index at acceptance

A2B 1B 1C 1D 1H 1JY 1K 1L 1S 1X

(72) Inventors ALEXANDR NIKOLAEVICH NESMEYANOV  
SERGEI VASILIEVICH ROGOZHIN  
VLADIMIR BORISOVICH TOLSTOGUZOV  
VLADIMIR IVANOVICH MISJUREV  
VERA ALEXANDROVNA ERSHOVA and  
EVGENY EVGENIEVICH BRAUDO(54) SYNTHETIC CAVIAR AND METHOD OF  
PREPARING SAME

(71) We, INSTITUT ELEMENTO-ORGANICHESKIH SOEDINENIY AKADEMII NEUK SSSR, of ulitsa Vavilova 28, Moscow, a State Enterprise organised and existing under the Laws of the Union of Soviet Socialist Republics (U.S.S.R.), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to foodstuffs, and more particularly to synthetic caviar imitating natural the caviar of sturgeon, salmon, and other valuable large fish: the invention also relates to methods of preparing same.

Known in the prior art is synthetic caviar composed of granules of an aqueous gel of edible gelatin which contains edible proteins and which is coated with a pellicle consisting of the products of tanning said gel with vegetable tannins. Said pellicle contains edible dyes, namely eno and annatto dyes, or complex salts of tri-valent iron and vegetable tannins. Eno and annatto dyes impart orange-red, and the complex salts of ferric iron and vegetable tannins a greyish-black colour to the pellicle of caviar granules. The granular mass of caviar contains various culinary additives, such as vegetable oil, sodium chloride, sodium glutamate and flavouring substances.

The described caviar is prepared by a method comprising preparing an aqueous gel of edible gelatin containing edible proteins; introducing said solution in the form of droplets into an edible oil the temperature of which, at least in its lower layers, is below the temperature at which the droplets of said solution congeal whereby granules of gelatin gel are produced, which contain edible proteins. The granules are washed with water to remove excess edible oil, and then treated with an aqueous solution of vegetable tannins, after which the caviar granules are washed with water to remove excess tannins and treated with aqueous solutions of edible dyes

(eno- and annatto dyes, or edible ferric salts). Then the caviar granules are given a culinary treatment comprising salting with sodium chloride and adding vegetable oil, flavouring substances, and other valuable substances that improve the nutritive properties of caviar.

Thus caviar obtained by this process has insufficient thermal stability since at temperature above 30°C gelatin gel melts and the granular structure of caviar is destroyed. This happens because, unlike in natural caviar, pellicles of artificial caviar have practically no mechanical strength. This is also the cause of difficulties that arise in storing, shipping and using caviar (prepared according to this method) at temperatures exceeding 30°C.

Attempts have been made to prepare food caviar having sufficient thermal stability. One such attempt produced a method which involved preparing an aqueous solution of edible gelatin containing edible proteins and acid polysaccharides; introducing said solution, in the form of droplets, into an edible oil, the temperature of which, at least in its lower layers, is below the temperature at which the droplets of said solution congeal. The shaped granules containing native proteins and acid polysaccharides are washed with water to remove the edible oil, and treated with aqueous solutions of edible salts of at least divalent metals (for example, calcium and/or aluminium). As a result of this treatment, a matrix of ionotropic gel is formed from the gel and the salts of acid polysaccharides with at least divalent metals (for example, calcium and/or aluminium). The granules of the mixed gel based on edible gelatin and the salts of said metals of acid polysaccharides, are treated with aqueous solutions of vegetable tannins. The obtained granules of caviar are washed with water to remove unreacted vegetable tannins, and then treated with an aqueous solution of edible dye (eno-, annatto dyes, or edible ferric salts). The granules of caviar are then given a culinary treatment comprising salting with sodium chloride and

50

55

60

65

70

75

80

85

90

adding vegetable oil, flavouring agents, and other culinary additives.

Said method is used to prepare synthetic caviar the granules of which are a mixed

5 aqueous gel of edible gelatin and salts of said metals (for example, calcium and/or aluminium) with acid polysaccharides, containing native proteins, and coated with a

10 pellicle consisting of the products of tanning of said gelatin gel with vegetable tannins. Said

15 pellicle contains edible dyes: eno-, annatto dyes, and complex salts of ferric iron and vegetable tannins. Eno- and annatto dyes give

20 orange-red colour, and complex salts of ferric iron and vegetable tannins greyish-black colour to the granule pellicles. The granular mass of caviar contains various culinary additives, such as sodium chloride, vegetable oil, flavouring agents, and other substances that improve

25 valuable properties of caviar.

Said caviar has sufficiently high thermal stability (not below 50°C) owing to the introduction into the gelatin gel of a matrix of a

30 gel of salts of acid polysaccharides. However, since the salts of acid polysaccharides have

35 high-melting point, they tend to deteriorate substantially the organoleptic properties of the

40 caviar in that the granules remain solid at the temperature of the oral cavity.

An object of this invention is to obviate or

mitigate the aforesaid disadvantages.

According to the present invention there is

provided synthetic caviar comprising granules of an aqueous gel of edible gelatin containing

45 edible protein wherein each granule is coated with two pellicles, namely an inner pellicle

50 consisting of the product of tanning of said gel with a vegetable tannin, and an outer

55 pellicle containing a calcium and/or aluminium salt of an acid polysaccharide.

Owing to mechanical strength of the outer

60 pellicle, consisting of acid polysaccharide salts, thermal stability of caviar granules increases to about 50°C. At the same time the organoleptic properties of natural caviar, including

65 the ability to be liquid at the temperature of the oral cavity, are preserved in the proposed

caviar.

It is preferable to use as the acid poly-

70 saccharide a water-soluble alginate or a low-

ester value pectin (ester value not higher than

75 50 per cent).

One of the preferred synthetic carriers of

80 the invention has the following composition (in grams per kg of caviar):

edible gelatin 40—80

edible proteins 55—140

vegetable tannins 2—6

salts of calcium and/or aluminium

of acid polysaccharides 0.1—2

water to make

60 one kg.

Higher nutritive properties are obtained in

the caviar by incorporating into the aqueous gel in addition to the edible proteins, the following substances, taken either separately or in various combinations, in the following quantities, in grams per kg of caviar:

1. lipids	3—70	65
2. carbohydrates	3—40	70
3. vitamins	0.001—0.02	

In the caviar of the invention, the aqueous gel of edible gelatin, or the inner pellicle consisting of the products of said tanning the gel, or both of them, can be coloured greyish-black.

Such colouration can be done by using ferric salts and vegetable tannins, for example, in any of the following ways:

(1) an aqueous gel of edible gelatin contains complex salts of ferric iron and vegetable tannins, in the quantity of 0.001—0.01 per kg of caviar;

(2) the inner pellicle, consisting of the products of tanning the gelatin, contains complex salts of ferric iron and vegetable tannins in the quantity of 0.001—0.01 g per kg of caviar, and the outer pellicle consists of salts of calcium and/or aluminium with acid polysaccharides, the quantity of the acid polysaccharide salts being 0.1—2 g per kg of caviar;

(3) the aqueous gel of gelatin and the inner pellicle consisting of the products of tanning said gel, contain complex salts of ferric iron and vegetable tannins in the quantity of 0.01 g per kg of caviar, and the outer pellicle, consisting of the calcium and/or aluminium salts of acid polysaccharides, contains also ferric salts of acid polysaccharides, the quantity of these salts of acid polysaccharides being 0.1—2 g per kg of caviar.

Said colour is given to the gel and/or the pellicle, consisting of the products of tanning said gel, by complex salts of ferric iron and vegetable tannins.

Moreover, the granules of aqueous gel can also be coloured orange-red. In this case the aqueous gel of edible gelatin and edible proteins, and if necessary other valuable additives such as lipids, carbohydrates, and vitamins, will contain also edible dyes-eno, and annatto dyes, taken in the quantity of 0.03—0.2 g per kg of caviar. Said dyes give orange-red colour to the aqueous gel.

The granular mass of the proposed caviar can also contain such substances as vegetable oil, sodium chloride, flavouring substances, preferably in the following quantities, (in grams per kg of caviar):

vegetable oil	10—100
sodium chloride	30—50
flavouring substances	3—30

- The mass may also contain 20—120 gm/kg of additional lipid. Moreover, the granular mass may also contain substances which improve the nutritive properties of the caviar namely from 3 to 30 grams per kg of caviar of indispensable amino acids, vitamins, antiseptics, taken either separately or in combinations.
- The invention also provides a method of preparing the synthetic caviar comprising preparing a 4 to 10 per cent aqueous solution of edible gelatin containing native proteins, introducing said solution in the form of droplets, into an edible oil the temperature of which, at least in its lower layers, is below the temperature at which the droplets of said solution congeal thus forming granules of gelatin gel which contain edible protein, washing the granules with water to remove edible oil, treating the washed granules with an aqueous solution of vegetable tanning substance, washing the tanned granules with water to remove unreacted vegetable tannins, and treating the washed granules with an aqueous solution of an acid polysaccharide, and with a solution of an edible calcium and/or aluminium salt thereby to form a calcium and/or aluminium salt of the acid polysaccharide.
- The calcium and/or aluminium salt of the acid polysaccharide imparts high thermal stability (to about 50°C) to the caviar. Preferably the acid polysaccharide is a water-soluble alginate or low-ester value pectin (ester value not higher than 50 per cent) in the form of their aqueous solutions of concentration of 0.1—0.5 per cent and pH from 3 to 7.
- To improve the nutritive properties of caviar, it is preferable to prepare a 4—10 per cent aqueous solution of edible gelatin containing, in addition to the edible proteins, also lipids, carbohydrates, and vitamins, taken either separately or in various combinations.
- As has already been said, in order to form the outer pellicle, the granules, after washing with water to remove excess vegetable tannin, are treated with an aqueous solution of an acid polysaccharide, and with an edible calcium and/or aluminium salt. Caviar granules can be treated first with the aqueous solution of acid polysaccharide, and then with aqueous solution of calcium and/or aluminium, or vice versa, i.e. first with the aqueous solutions of a calcium and/or aluminium salt and then with aqueous solution of acid polysaccharide.
- The proposed method makes it possible to prepare aqueous gels coloured greyish-black or orange-red.
- If the aqueous gel of gelatin is to be coloured greyish-black, edible dyes—ferric salts of edible acids and vegetable tannins may be added to the 4—10 per cent aqueous solution of edible gelatin containing edible proteins and, if desired, other valuable substances such as lipids, carbohydrates, and vitamins. Complex salts of ferric iron and vegetable tannins that are formed as a result of this process, give to the aqueous gel of edible gelatin a greyish-black colour resembling that of the natural caviar of sturgeon.
- If the aqueous gel of edible gelatin is to be coloured orange-red, edible dyes, such as eno or annatto dyes may be added during preparation the starting 4—10 per cent aqueous solution of edible gelatin containing edible proteins and, if desired, the above-named valuable additives. The eno, and annatto dyes give the gelatin gel an orange-red colour imitating that of caviar of salmon.
- Alternatively the inner pellicle, consisting of the products of tanning of the gelatin gel, may be coloured in greyish-black tint by using an aqueous solution of an edible ferric salt.
- It should also be noted that after having washed the caviar granules with water to remove unreacted vegetable tannins, the operations that follow, namely, treatment with the aqueous solution of an acid polysaccharide, treatment with a calcium and/or aluminium salt, and treatment with an aqueous solution of an edible ferric salt can be in any order. The sequence, in which these operations follow, does not affect the quality of the end product. Below follow some of the possible versions of sequences of said operations.
- Version one: after washing to remove unreacted vegetable tannin, caviar granules are treated with an aqueous solution of acid polysaccharides, and then with an aqueous solution containing an edible salt or calcinn and/or aluminium and edible ferric salt.
- Version two: after having been washed to remove excess vegetable tannin, caviar granules are treated first with an aqueous solution containing edible calcium and/or aluminium salts and edible ferric salt and then with aqueous solutions of acid polysaccharide.
- Version three: after having been washed to remove excess vegetable tannin, caviar granules are treated first with aqueous solutions of acid polysaccharide, and then the caviar granules are given consecutive treatment with an aqueous solution of an edible ferric salt and an aqueous solution of edible calcium and/or aluminium salts.
- Version four: after having been washed to remove excess vegetable tannin, caviar granules are treated first with aqueous solutions of an edible ferric salt, and then consecutively with an aqueous solution of an acid polysaccharide and an aqueous solution of edible calcium and/or aluminium salts.
- Both, coloured and uncoloured caviar granules, may be given a culinary treatment consisting of salting with sodium chloride and adding vegetable oil, and flavouring substances. Moreover, other valuable additives which improve the nutritive properties of the

caviar, such as lipids, indispensable amino acids, vitamins, and antiseptics, can be added to the granular mass of caviar at the stage of the culinary treatment, either separately or in various combinations.

Thus, the proposed method makes it possible to prepare synthetic caviar which resembles natural caviar of sturgeon, salmon, and other valuable large fish, with respect to its taste and colour.

The following Examples are given by way of illustration of the invention.

#### Example 1

100 kg of a 7 per cent aqueous solution of food gelatin containing edible casein was prepared by dissolving 15 kg of casein in a 0.1N aqueous solution of sodium hydroxide at a temperature of 50—60°C with mixing for 1—2 hours. Into the prepared casein solution there is added with stirring 7 kg of edible gelatin in the form of a 20—30 per cent solution in water. Stirring is continued for another 30—60 minutes at a temperature of 50—60°C.

25 The prepared solution is introduced, in the form of droplets, into corn oil, the temperature of which in its lower layers is below the temperature at which the droplets of said solution congeal, namely 4—7°C. Under these conditions, the droplets of the starting solution form regular spheres of 2—4 mm in diameter. When cooled in the lower layers of corn oil the gelatin gels to form granules.

30 The granules of gelatin gel containing casein are washed with water to remove excess corn oil. Washing is performed with stirring for 3—5 minutes at a temperature of 4—15°C. The granules are then separated from water and treated with an aqueous solution of vegetable tannins which is prepared by boiling 15—20 kg of green tea, or finely cut tea leaves, in 350 litres of water for 60 minutes. The extract of tannin is cooled before use to 4—10°C. The granules are treated with this solution at a temperature of 4—10°C for 20—35 minutes. As a result, a dense, slightly yellow pellicle, consisting of the products of tanning the gelatin gel with vegetable tannins, is formed on the surface of the granules.

35 On the termination of the tanning process, caviar granules are washed with water to remove the unreacted vegetable tanning substances, for 5—7 minutes with stirring at a temperature of 7—15°C. The washed granules are treated with a 0.1 per cent aqueous solution of an acid polysaccharide — sodium alginate, having a pH 5—6, at a temperature of 4—15°C for 15 minutes. The granules are then separated from the sodium alginate solution and treated for 2—5 minutes with a 0.3—0.8 per cent aqueous solution of calcium acetate having a pH 4—5, at a temperature of 4—15°C. As a result of this

treatment of caviar granules with the aqueous solution of acid polysaccharide and calcium acetate, another, outer pellicle, consisting of calcium alginate, is formed on the caviar granules to give them high thermal stability.

40 Caviar granules are washed with water under stirring for 2—3 minutes at a temperature of 4—15°C. The yield is 105—115 kg of product (the gain in weight, with respect to the weight of the starting 7 per cent aqueous solution of food gelatin is due to granule swelling in aqueous media).

45 The obtained synthetic caviar (uncoloured, with granules enclosed in two pellicles) contains the following components, in grams per kg of caviar:

edible gelatin	60—65
casein	130—140
vegetable tannins	2—4
calcium alginate	0.1—1
water	to make one kg.

50 The tests have shown that caviar granules remain stable for 60 minutes at temperature exceeding the point at which gelatin gel melts i.e. 35°C.

#### Example 2

55 Synthetic caviar, (uncoloured, with granules enclosed in two pellicles) is prepared by a procedure similar to that described in Example 1, except that an 0.2 per cent aqueous solution of a low-ester value pectin (ester value 40 per cent) having a pH 4—5, is used instead of an 0.1 per cent aqueous solution of sodium alginate.

60 The obtained caviar remains solid for 45 minutes at a temperature exceeding that at which gelatin gel melts, i.e. 40°C.

#### Example 3

65 Synthetic caviar (uncoloured, with granules enclosed in two pellicles) is prepared by a procedure described in Example 1, except that a mixture of an 0.1 per cent aqueous solution of sodium alginate and an 0.15 per cent aqueous solution of low-ester value pectin (ester value 40 per cent), having a pH 3—4, are used instead of the aqueous solution of acid polysaccharide.

#### Example 4

70 100 kg of an 8 per cent aqueous solution of food gelatin containing a mixture of edible proteins, lipids, and carbohydrates, namely, a mixture of casein and dried milk are prepared. To that end, 5 kg of casein are dissolved in an 0.1N aqueous solution of sodium hydroxide at a temperature of 50—60°C with stirring for 1—2 hours. Into the obtained casein solution there are added 10 kg of dried milk and 8 kg of gelatin in the form of a 20—30 per cent aqueous solution. The mixture is

stirred for 30—60 minutes at a temperature of 50—60°C.

The obtained solution is introduced, in the form of droplets, into a mixture of one part of corn oil and two parts of cotton-seed oil, the temperature of which in its lower layers is below the point at which the droplets congeal, namely at the temperature of 4—7°C. Under these conditions, the solution droplets form regular spheres of 2—4 mm in diameter. As they are cooled, gelatin converts into gel.

The shaped gelatin granules containing edible proteins (casein, lactalbumin, lactoglobulin, and others), and also lipids and carbohydrates, are washed with water to remove oil. Washing is continued for 3—5 minutes at a temperature of 4—10°C, with stirring. The granules are separated from water and treated with 300 litres of a 0.3—0.5 per cent aqueous solution of vegetable tannins, which is prepared by dissolving in water a dry preparation of vegetable tannins (tea tannides). The tanning process is continued for 20—30 minutes at a temperature of 4—10°C, with stirring, until a dense, slightly yellow pellicle, consisting of the products of gel tanning with vegetable tannins, is formed on the granule surface.

After tanning, the caviar granules are washed with water from unreacted tannins at a temperature of 7—15°C for 3—5 minutes with stirring. Then the granules are treated with an 0.1 per cent aqueous solution of acid polysaccharide—gum arabic, having a pH 4—6, at a temperature of 4—15°C for 15 minutes. The granules are then separated from the solution of gum arabic, and treated for 5—7 minutes at a temperature of 4—15°C and a pH 4—5, with a 0.1—0.15 per cent aqueous solution of calcium acetate. As a result of this treatment with the aqueous solution of acid polysaccharide and calcium acetate, an outer pellicle consisting of a calcium salt of gum arabic, is formed on the surface of the pellicle to give high thermal stability to caviar granules.

The obtained caviar granules are washed with water at a temperature of 4—15°C and for 3—5 minutes with stirring. The yield is 50 115 kg of the product.

The obtained caviar (uncoloured, coated with two pellicles) contains the following components (in grams per kg of caviar):

55	edible gelatin	70
	casein	45
	other edible proteins (lactalbumin, lactoglobulin, etc)	20
	lipids	25
	carbohydrates	15
60	vegetable tannins	2—4
	calcium salt of arabic gum	0.1—1
	water	to make one kg.

The thermal stability of the product is the same as in Example 1.

65

#### Example 5

There are prepared 100 kg of a 10 per cent aqueous solution of food gelatin containing casein (edible protein) and starch (carbohydrates). To that end, 12 kg of casein are dissolved in an 0.1N aqueous solution of sodium hydroxide at a temperature of 50—60°C with stirring for 1—2 hours. Into the obtained solution, containing casein and gelatin, 5 kg of soluble starch are added, and the components are mixed for 30—60 minutes at a temperature of 50—60°C.

70

The obtained solution is introduced, in the form of droplets, into a mixture of equal volumes of corn oil and cotton-seed oil, the temperature of which in the lower layers is below the point at which the droplets congeal, namely the temperature of 3—5°C. Under these conditions, the solution droplets form regular spheres of 2—4 mm in diameter. As they are cooled in the lower layers of oil, gelatin converts into gel.

75

The shaped granules of gelatin gel, containing casein and starch, are washed with water from residual oil at a temperature of 4—15°C for 3—5 minutes, with stirring. The granules are then separated from water and treated with an aqueous solution of vegetable tanning substances which is prepared by boiling 40—45 kg of finely cut coarse tea leaves (or waste material obtained in seasonal tea bush cutting) in 300 litres of water for 60 minutes. The solution of vegetable tannins is cooled before use to 4—7°C. The granules are treated with this solution at a temperature of 4—15°C, with stirring, for 20—35 minutes. As a result of this treatment, a dense, slightly yellowish coat consisting of the product of gelatin gel tanning with vegetable tannins, is formed on the surface of granules.

90

After completion of the tanning process, caviar granules are washed with water from unreacted tannins for five minutes with stirring at a temperature of 7—15°C. The washed granules are treated with a 1 per cent aqueous solution of calcium chloride at a temperature of 4—15°C for ten minutes. The granules are then separated from calcium chloride solution and treated for 15 minutes at a temperature of 4—15°C and a pH 4—6 with an 0.2 per cent aqueous solution of a mixture of sodium alginate and low-ester value pectin (ester value 40 per cent) taken at the weight ratio of 1:1. As a result of this treatment of caviar granules with the aqueous solution of acid polysaccharides and calcium chloride, an outer pellicle, consisting of calcium alginate and calcium pectinate, is formed on the caviar granules, to give them high thermal stability. On the termination of processing the caviar granules with the aqueous solution of a mixture of sodium

95

100

105

110

115

120

125

alginate and pectin, the granules are washed with water. The yield of product is 125 kg.

Synthetic caviar thus obtained contains the following components (in grams per kg of caviar):

	edible gelatin	60
	casein	95
	starch	40
	vegetable tannins	3—5
10	calcium alginate and calcium pectinate	0.3—0.6
	water	to make one kg.

Thus-obtained food caviar remains solid at a temperature of 50°C for thirty minutes.

#### Example 6

Synthetic caviar (uncoloured, with granules enclosed in two pellicles) is prepared by a procedure described in Examples 1, 2 and 3, except that before mixing with the aqueous solution of gelatin, cod-liver oil is added to the casein solution in the quantity of 0.3—6 kg, which corresponds to 3—57 g per kg of caviar.

#### Example 7

Synthetic caviar (uncoloured, with granules enclosed in two pellicles) is prepared by a procedure similar to that described in Examples 1, 2, and 3, except that before mixing with the aqueous solution of gelatin, starch is added to the casein solution in the quantity of 0.3—3 kg, which corresponds to 3—27 g per kg of caviar.

#### Example 8

Synthetic caviar (uncoloured, with granules enclosed in two pellicles) is prepared by a procedure similar to that described in Examples 1, 2, and 3, except that before mixing with the aqueous solution of gelatin, cod-liver oil in the quantity of 0.3—6 kg, and starch in the quantity of 0.4—4 kg are added to the casein solution, which corresponds to 3—57 g of cod-liver oil and 4—38 g of starch per kg of caviar.

#### Example 9

There are prepared 100 kg of a 10 per cent aqueous solution of food gelatin containing edible proteins and lipids (casein and edible vegetable oil).

To that end, stable emulsion of vegetable oil in a casein solution is first prepared by mixing 45 kg of a 10 per cent solution of casein in an 0.1N aqueous solution of sodium hydroxide and 13 kg of an 0.1 per cent aqueous solution of low-ester value pectin (ester value 40 per cent). At the same time, emulsion of 0.8 kg of an 0.2 per cent aqueous solution of calcium acetate in a mixture with 4.3 kg of corn oil and 4.3 kg of cotton-seed

oil is prepared. The emulsion of calcium acetate solution in vegetable oil is introduced with stirring into a solution of casein and pectin to prepare the emulsion, in which the continuous phase is the casein solution and the dispersed phase is the mixture of corn oil and cotton-seed oil. The volume ratio of the dispersed and the continuous phases is 0.15:1. The role of the emulsion stabilizer is performed by calcium pectinate which forms protective coats on the particle surfaces to keep them from coalescing. The emulsifying conditions are selected so that the viscosity of the emulsion at 20°C is 100—200 centipoise. The obtained emulsion does not delaminate on storage in a refrigerator at a temperature of 4—8°C for 20 days.

Into the prepared emulsion are added 10 kg of gelatin in the form of a 20—30 per cent aqueous solution to prepare a 10 per cent aqueous solution of gelatin containing casein and edible vegetable oils (corn and cotton-seed oil). Further operations for preparing synthetic caviar are the same as described in Example 1.

The process yields 125 kg of uncoloured caviar coated with two pellicles, which remains solid at a temperature of 40°C for 45 minutes. The granule contents do not delaminate during storing in a refrigerator at a temperature of 4—8°C for two weeks.

Thus-obtained caviar contains the following components, in grams per kg of caviar:

edible gelatin	80
casein	35
vegetable oils	70
vegetable tannins	2—4
calcium alginate and calcium pectinate	1.5—2
water	to make one kg.

#### Example 10

Synthetic caviar (uncoloured, coated with two pellicles) is prepared by a procedure similar to that described in Example 9, except that in preparing food emulsion an 0.1 per cent aqueous solution of sodium alginate is used instead of an 0.1 per cent aqueous solution of low-ester value pectin.

#### Example 11

Synthetic caviar (uncoloured, with granules enclosed in two pellicles) is prepared by a procedure as described in Examples 9 and 10, except that about 50 per cent by volume of vegetable oil in the emulsion is replaced by cod-liver oil.

#### Example 12

Synthetic caviar (uncoloured, with granules enclosed in two pellicles) is prepared by a procedure described in Examples 1, 2 and 3, except that dry defatted milk, in the quantity of 15 kg, is added instead of casein. This component is dispersed in water and then

10 kg of food gelatin, in the form of a 20—30 per cent aqueous solution, are added.

**Example 13**

Synthetic caviar (uncoloured, with granules enclosed in two pellicles) is prepared by a procedure described in Example 12, except that cod-liver oil, in the quantity of 0.3—6 kg, is added to the dispersion of dry milk in water.

**Example 14**

Synthetic caviar (uncoloured, with granules enclosed in two pellicles) is prepared by a procedure described in Examples 1, 2 and 3, except that condensed milk (without sugar), in the quantity of 80 kg, is used instead of casein solution. Into this component, are added with stirring 6 kg of food gelatin at a temperature of 40—60°C, (the gelatin having preliminarily been dissolved in 14 litres of water at a temperature of 40—50°C). The obtained solution has the density of 1.07 at 40°C and the viscosity of 79 centipoise at 40°C.

The caviar prepared in this example remains solid at a temperature of 35°C for 60 minutes.

**Example 15**

Synthetic caviar (uncoloured, with granules enclosed in two pellicles) is prepared by a procedure similar to that described in Example 14, except that soya-bean milk, in the quantity of 79—79.9 kg, is used instead of sugar-free condensed milk. To the soya milk added is 0.3—1 kg of cod-liver oil, and then, to the obtained mixture, added with stirring are 6 kg of food gelatin pre-dissolved in 14 litres of water.

**Example 16**

Synthetic caviar (uncoloured, with granules enclosed in two pellicles) prepared in Example 1, is subjected to a culinary treatment to give it the organoleptic properties resembling those inherent in natural caviar. The treatment consists in the following.

Granules coated with two pellicles are kept for five minutes at a temperature of 4—15°C in a 4—6 per cent aqueous solution of sodium chloride. After salting, 0.3 per cent by weight of sodium glutamate, 1 per cent by weight of corn oil, and 2.7 per cent by weight of herring flesh finely disintegrated in corn oil, are added to the granular mass to prepare 112—122 kg of caviar.

The obtained caviar contains the following components, in grams per kg of caviar:

edible gelatin	57—64	
casein	125—135	
vegetable tannins	2—4	
calcium alginate	0.1—1	
sodium chloride	30	
herring flesh	27	
sodium glutamate	3	
corn oil	10	
water	to make one kg.	

**Example 17**

Synthetic caviar (uncoloured, with granules enclosed in two pellicles) prepared in Example 5, is treated to give it the organoleptic properties resembling those inherent in natural caviar. The culinary treatment consists in the following.

Granules coated with two pellicles are salted as described in Example 16. Then 0.3 per cent by weight of sodium glutamate, and 12 per cent by weight of emulsion containing casein, corn oil, cod-liver oil, and also flavouring substances, are added to the salted granules.

The method of preparing the emulsion consists in the following. Mixed together are 200 ml of a 15 per cent casein solution in an 0.1N aqueous solution of sodium hydroxide, 100 ml of an 0.1 per cent aqueous solution of beet pectin (or an 0.1 per cent aqueous solution of sodium alginate), 0.06 g of flavouring substances (namely 0.4 g of sodium inosinate, 0.33 g of maltol, 0.33 g of L-tryptophan) and 0.9 ml of alcoholic solution of aromatic substances of the following composition (in per cent by weight):

trimethylamine	4.9	
triethylamine	9.5	
pyridine	1.9	
piperidine	4.8	95
n - propylamine	4.8	
undecanone - 2	1.9	
diethylacetal of n - valeric aldehyde	4.8	
ethyl alcohol	67.4	100

At the same time, 500 ml of corn oil (or its mixture with cotton-seed oil at the volume ratio of 1:1) are mixed with 150 ml of cod-liver oil and 50 ml of an 0.2 per cent aqueous solution of calcium acetate and the mixture is emulsified. The prepared emulsion is introduced, in a thin jet, into the solution containing casein, pectin, and flavouring additives. The emulsifying conditions are so selected that the finished emulsion has a viscosity of 100—200 centipoise at 20°C.

The prepared emulsion does not delaminate during storage in a refrigerator at a temperature of 4—8°C for twenty days.

The yield of product is 140 kg. The obtained caviar contains the following components, in grams per kg of caviar:

edible gelatin	70	
casein	89	
(of this quantity 85 g in the aqueous gel of gelatin and 4 g in granular mass of caviar)		120
starch	35	
vegetable tannins	4—6	125
calcium alginate and calcium pectinate	0.5—1	

8	1,474,891	8
	sodium chloride	30
	sodium glutamate	3
	sodium inosinate	0.048
	maltool	0.040
5	L - tryptophan	0.040
	flavouring agents	0.036
	ethyl alcohol	0.07
	corn oil	60
	cod-liver oil	18
10	water	to make one kg.
	edible gelatin	52-56
	casein	110-120
	vegetable tannins	3-5
	calcium alginate	0.3-0.6
	sodium chloride	50
	sodium glutamate	3
	sodium inosinate	0.04
	maltool	0.03
	L - tryptophan	0.03
	flavouring substances	0.02
	ethyl alcohol	0.04
	corn oil	100
	cod-liver oil	20
	amino acids, including indis- pensable amino acids, and peptides (yeast hydrolyzate)	75
15	sorbic acid	28
	ascorbic acid	1
	water	1
		to make one kg.

The finished product, caviar, resembles natural caviar of sturgeon with respect to its taste and odour; its consistency is slightly loose. The granules remain solid at a temperature of  $40^{\circ}\text{C}$  for 45 minutes.

**Example 18**

Synthetic caviar (uncoloured, with granules enclosed in two pellicles) is prepared by a procedure described in Example 17, except that in order to prevent caviar from bacterial contamination, it is treated, after salting, with an aqueous solution of formaldehyde, having a concentration of 0.01—1 per cent, for 0.5—5 minutes, the ratio of the weight of granules to the weight of the formaldehyde solution being from 1:0.5 to 1:10.

### **Example 19**

30 Synthetic caviar (uncoloured, with granules enclosed in two pellicles) prepared as described in Example 1, is treated to give it the organoleptic properties resembling those of natural caviar, and also to increase its biological values and to preserve from bacterial contamination. The culinary treatment consists  
35 in the following.

Caviar granules coated with two pellicles are kept for four minutes at a temperature of 4-15°C in an aqueous solution containing 20 per cent by weight of yeast hydrolyzate and 4-6 per cent by weight of sodium chloride. This increases the dry weight of caviar granules on account of diffusion, into the granules, of amino acids, including indispensable amino acids, peptides, and sodium chloride, and also on account of partial hydration of the granules. Thus-treated granules are separated from liquid. Then, added to the granules are 0.3 per cent by weight of sodium glutamate, 0.1 per cent by weight of sorbic acid, 0.1 per cent by weight of ascorbic acid, 2 per cent by weight of cod-liver oil, 10 per cent by weight of corn oil, 0.004 per cent by weight of sodium inosinate, 0.003 per cent by weight of maltol, 0.003 per cent by weight of L-tryptophan, and 0.006 per cent by weight of alcoholic solution of flavouring additive. The composition of the flavouring additive is specified in Example 17.

The yield of the process is 125—135 kg of caviar containing the following components, in grams per kg of caviar:

The finished product resembles natural caviar of sturgeon with respect to its taste and odour. Its granules remain solid at a temperature of 50°C for fifteen minutes.

#### Example 20

Synthetic caviar (uncoloured, with granules enclosed in two pellicles) is prepared as described in Examples 1 and 2, except that an 0.2-1 per cent aqueous solution of aluminium potassium sulphate or aluminium ammonium sulphate, having a pH 3.8-4.2, is used instead of the aqueous solution of calcium acetate.

The resultant product is caviar having the outer pellicle of aluminium alginate or aluminium pectinate.

### Example 21

**Example 21**

Synthetic caviar (uncoloured, with granules enclosed in two pellicles) is prepared by a procedure described in Examples 1 and 2, except that an aqueous solution containing calcium chloride and aluminium chloride, and having a pH 4, is used instead of the aqueous solution of calcium acetate. The total concentration of salts is 0.8 per cent; the ratio of concentrations of  $\text{Ca}^{2+}$  to  $\text{Al}^{3+}$  ions (in gram-ions) is 2 : 1.

The resultant product is synthetic caviar the granules of which have the outer pellicle formed by the alginate or pectinates of calcium or aluminium.

### Example 22

Synthetic caviar (uncoloured, with granules enclosed in two pellicles) is prepared by a procedure similar to that described in Examples 1 and 2, except that an 0.1-0.3 per cent aqueous solution of aluminium chloride, having a pH 3.8-4.2, is used instead of the aqueous solution of calcium acetate.

The resultant product is synthetic caviar the granules of which have the outer pellicle

formed by aluminium alginate or aluminium pectinate.

#### Example 23

Synthetic caviar is prepared by a procedure similar to that described in Example 9, except that 4.2—84 g of vitamin A concentrate, having an activity of 100,000 International Units per gram of the concentrate, are added to the mixture of corn oil and cotton-seed oil. One kg of the finished product contains 0.001—0.02 g of vitamin A.

#### Example 24

Synthetic caviar is prepared by a procedure similar to that described in Example 17, except that 5 g of vitamin A concentrate, having an activity of 100,000 IU per gram of the concentrate, are added to the vegetable oil used for preparing emulsion. One kg of the finished product contains 0.0011 g of vitamin A.

#### Example 25

There are prepared 100 kg of a 7 per cent aqueous solution of food gelatin containing casein. To that end, 15 kg of casein are dissolved with stirring for one hour in an 0.1N solution of sodium hydroxide at a temperature of 50—60°C. Into the obtained solution of casein, added with stirring are 7 kg of food gelatin in the form of a 20—30 per cent aqueous solution. The mixture is then stirred for another hour at a temperature of 50—60°C.

The obtained starting solution having a pH 6.2 is passed through a fabric filter and introduced, in the form of droplets, into petroleum oil of pharmaceutical grade. The upper layer of the oil is heated to the temperature of 25—40°C and the lower is cooled to the temperature of 4—10°C. Under these conditions, the droplets of the starting solution assume the regular form of a sphere 2—4 mm in diameter. As they are cooled, gelatin is converted in to gel.

The shaped granules of gel containing casein are washed with water from oil at a temperature of 4—10°C for 3—5 minutes. The granules are then separated from water and treated with an aqueous solution of vegetable tannins which is prepared by boiling 15—20 kg of green tea in 300 litres of water for one hour. The solution is cooled to 4—10°C before use. Caviar granules are treated with this solution by keeping in it at a temperature of 4—10°C with stirring for 25—30 minutes. A dense, slightly yellowish coat, consisting of the products of gel tanning with vegetable tanning substances, is formed on the granules as a result of this treatment.

On the termination of the tanning process, caviar granules are washed with water to remove unreacted tannins at a temperature of 4—10°C with stirring for 3—5 minutes. The

washed granules are treated for 1—2 minutes with an 0.1 per cent solution of ferric chloride at a temperature of 4—10°C with stirring. As a result of this treatment, the pellicle consisting of the products of gel tanning is coloured greyish-black due to the formation of complex salts of ferric iron and vegetable tannins.

Coloured caviar granules are separated from ferric chloride solution, washed with water for three minutes at a temperature of 4—10°C and then treated with an 0.25 per cent aqueous solution of low-ester value pectin (the ester value 20—40 per cent) having the pH 4.5—5.5. This treatment is performed at a temperature of 4—10°C for 10—15 minutes. Then the caviar granules are washed with water at a temperature of 4—10°C for 1—5 minutes and treated with a 1 per cent aqueous solution of calcium acetate at a temperature of 4—10°C for 3—5 minutes. As a result of the treatment of caviar granules with the aqueous solution of pectin and calcium acetate, another, outer pellicle, consisting of calcium pectinate, is formed on the caviar granules to give them higher thermal stability.

After separation of caviar granules from the solution of calcium acetate, caviar granules, coated with two pellicles, are washed with water at a temperature of 4—10°C for 3—5 minutes. The resultant product weighs 115 kg and contains the following components, in grams per kg of caviar:

edible gelatin	60	95
casein	130	
vegetable tannins	2—3	
ferric pectinate and calcium pectinate	0.1—0.6	
complex salts of ferric iron and vegetable tannins	0.003—0.007	100
water	to make one kg.	

The product remains solid at a temperature of 40°C for one hour and resembles natural caviar of sturgeon with respect to colour. 105

#### Example 26

Synthetic caviar, prepared by a procedure described in Example 25, is given a culinary treatment consisting in the following.

Caviar granules coated with two pellicles are washed with a 3—7 per cent aqueous solution of sodium chloride at a temperature of 4—10°C for 3—5 minutes. Then, with stirring, there are added 0.2—0.5 per cent by weight of sodium glutamate, 0.1 per cent by weight of sorbic acid, 0.1 per cent by weight of ascorbic acid, 0.01—0.1 per cent by weight of sodium inosinate, 2—7 per cent by weight of dry milk, 4—10 per cent by weight of a mixture of equal parts of corn oil and cotton-seed oil, 5 per cent by weight of cod-liver oil, 0.3—1.5 per cent by weight of herring juice, and 1—2.5 per cent by

weight of soya-bean protein hydrolyzate. The resultant product weighs 132—146 kg. The obtained caviar contains the following components, in grams per kg of caviar:

5	edible gelatin	48—53
	casein	100—105
	vegetable tannins	2—4
	calcium pectinate and ferric pectinate	0.4—0.7
10	complex salts of ferric iron and vegetable tannins	0.003—0.007
	sodium chloride	40
	herring juice	3—15
15	sodium glutamate	2—5
	sodium inosinate	0.1—1
	corn oil	20—50
	cod-liver oil	50
	dried milk	20—70
	hydrolyzate of soya-bean protein	10—25
20	ascorbic acid	1
	water	to make one kg.

25 The product remains solid at a temperature of 40°C for one hour and well imitates the colour and taste of natural caviar of sturgeon.

#### Example 27

30 Synthetic caviar imitating natural caviar of sturgeon is prepared by the procedure described in Example 25, except that an 0.1—0.2 per cent aqueous solution of sodium alginate, having the pH 4—6, is used instead of the aqueous solution of pectin.

35 The resultant product is synthetic caviar the granules of which are coated with the outer pellicle consisting of calcium alginate and ferric alginate.

#### Example 28

40 Synthetic caviar imitating natural caviar of sturgeon is prepared by a procedure similar to that described in Example 25, except that an 0.1 per cent aqueous solution of gum arabic having the pH 6—7, is used instead of the aqueous solution of pectin, and an 0.3 per cent aqueous solution of ferric malate is used instead of the aqueous solution of ferric chloride.

50 The resultant caviar has its granules coated with the outer pellicle consisting of calcium salts and ferric salt of gum arabic.

#### Example 29

55 There are prepared 100 kg of a 5 per cent aqueous solution of food gelatin containing casein. To that end 14 kg of casein are dissolved in an 0.1N aqueous solution of sodium hydroxide at a temperature of 50—60°C with stirring for two hours. Into the obtained solution, added with stirring are 5 kg of edible gelatin in the form of a 20—30

per cent aqueous solution. The mixture is then stirred for another 50—60 minutes at a temperature of 50—60°C.

The obtained starting solution, having a pH 6.1—6.3, is passed through a fabric filter and introduced, in the form of droplets, into cotton oil, the upper layer of which is heated to the temperature of 30—45°C, while its lower layers are cooled to 5—8°C. Under these conditions, the droplets of the starting solution form regular spheres having 2—4 mm in diameter. As they pass through the upper layers the viscosity of which is reduced by heating the droplets quickly pass them to reach the lower, cool layers of oil where the gel of gelatin, containing casein, is converted into gel.

70 The shaped granules of gelatin gel are washed with water from cotton oil at a temperature of 4—10°C with stirring for five minutes. Then the granules are treated with an aqueous solution of vegetable tannins which is prepared by boiling 15—20 kg of tea dust (waste of production of green tea) in 300—400 litres of water for one hour. The solution is cooled before use to the temperature of 4—8°C. The granules are treated with this solution at a temperature of 4—8°C with stirring for 15—25 minutes. As a result of this treatment a dense, slightly yellowish pellicle consisting of the products of gel tanning with vegetable tannins, is formed on the granule.

90 After tanning, the granules are washed with water to remove unreacted tannins at a temperature of 4—8°C for 3—5 minutes. The washed granules are treated for 3—5 minutes at a temperature of 4—10°C under stirring with an 0.1 per cent aqueous solution of ferric iron, containing 0.5 per cent of calcium chloride and having the pH 4—5. As a result, the pellicle consisting of the products of gel tanning is coloured greyish-black. The colour is due to the formation of complex salts of ferric iron and vegetable tannins.

100 Caviar granules coated with a coloured pellicle, are separated from the solution of salts of iron and calcium, washed with water at a temperature of 4—10°C for three minutes and treated with a 0.2 per cent aqueous solution of a low ester value pectin (ester value 40 per cent) having a pH 5.3—5.5. The treatment is carried out at a temperature of 4—15°C with stirring for 15 minutes. As a result of this treatment, another, outer pellicle consisting of ferric pectinate and calcium pectinate, is formed on the granule to give high thermal stability to caviar.

110 Caviar granules coated with two pellicles are washed with a 4—6 per cent aqueous solution of sodium chloride at a temperature of 4—15°C for five minutes (salting). Then, added to the granules are 0.3 per cent by weight of sodium glutamate, 0.1 per cent by weight of sorbic acid, 0.1 per cent by weight of ascorbic acid, 2.8 per cent by weight of

65

70

75

80

85

90

95

100

105

110

115

120

125

hydrolyzate of soya-bean protein, 10 per cent by weight of corn oil, and 4 per cent by weight of herring flesh finely disintegrated in corn oil. The resultant product is 122 kg of caviar containing the following components, in grams per kg of caviar:

	edible gelatin	40
	casein	115
	vegetable tannins	3—4
10	calcium pectinate and ferric pectinate	0.3—0.8
	complex salts of ferric iron and vegetable tannins	0.001—0.005
15	sodium chloride	45
	sodium glutamate	3
	herring flesh	4
	corn oil	100
	hydrolyzate of soya-bean protein	28
20	sorbic acid	1
	ascorbic	1
	water	to make one kg.

The finished product resembles natural caviar of sturgeon with respect to its taste and appearance. Caviar granules remain solid at a temperature of 35—40°C for one hour.

#### Example 30

Synthetic caviar, imitating natural caviar of sturgeon, is prepared by a procedure similar to that described in Example 29, except that an 0.1—0.2 per cent aqueous solution of sodium alginate having a pH 5—6 is used instead of the aqueous solution of pectin.

The resultant caviar has granules, the outer pellicle of which, is formed by calcium alginate and ferric alginate.

#### Example 31

Synthetic caviar resembling natural caviar of sturgeon is prepared by a procedure similar to that described in Example 29, except that a 0.2 per cent aqueous solution of gum arabic, having a pH 6—7, is used instead of the aqueous solution of pectin.

The resultant caviar has granules, the outer pellicle of which, is formed by calcium and ferric salts of gum arabic.

#### Example 32

Synthetic caviar resembling natural caviar of sturgeon is prepared by a procedure similar to that described in Example 29 except that after, treatment with an aqueous solution containing a mixture of ferric chloride and calcium chloride, caviar granules are treated with an aqueous solution containing a mixture of 0.1 per cent by weight of sodium alginate and 0.15 per cent by weight of low-ester value pectin (ester value 40 per cent), instead of treatment with the aqueous solution of low-ester value pectin.

The resultant caviar has granules, the outer pellicles of which, are formed by alginates and pectinates of calcium and tervalent iron.

#### Example 33

Prepared are 100 kg of a 7 per cent aqueous solution of food gelatin containing casein. To that end 17 kg of casein are dissolved at a temperature of 50—60°C with stirring in an 0.1N aqueous solution of sodium hydroxide for 1—2 hours. Into the obtained casein solution are added, at a temperature of 50—60°C, with stirring, 7 kg of food gelatin in the form of a 20—30 per cent aqueous solution. Stirring at the temperature of 50—60°C is continued for another hour.

The obtained starting solution containing gelatin and casein is introduced, in the form of droplets, into corn oil, the lower layers of which are cooled to 4—7°C. Under these conditions the droplets of the starting solution form regular spheres 2—4 mm in diameter, and gelatin is converted at this temperature into gel.

The shaped granules containing casein, are separated from oil and washed with water at a temperature of 4—15°C for 3—5 minutes. The granules are then treated with an aqueous solution of vegetable tannins which is prepared by dissolving in water a dry preparation of vegetable tannins (tea tannides). The tanning process is carried out at a temperature of 4—15°C for 20—25 minutes. As a result, a dense, slightly yellowish pellicle consisting of the product of gel tanning, is formed on the granule.

On the termination of the tanning process, caviar granules are washed with water to remove unreacted tannins. The washing is performed at a temperature of 4—15°C for 3—5 minutes. The granules are then treated with a 0.2—0.3 per cent aqueous solution of ferric lactate (pH of the solution 4—5) containing 0.2—1 per cent of calcium acetate. The process temperature is 4—15°C, the duration 2—5 minutes. As a result of this treatment, the pellicle, consisting of the products of gel tanning, is coloured greyish-black with a brownish tint.

The granules coated with coloured pellicles are separated from the solution of iron and calcium salts, washed with water, and treated with a 0.2 per cent aqueous solution of sodium alginate having a pH 4—5. The process temperature is 4—15°C, the duration is ten minutes. An outer pellicle, consisting of calcium alginate and ferric alginate, is formed on the granules as a result of this treatment. The outer pellicle gives the granules high thermal resistance.

The obtained caviar granules are given a culinary treatment consisting in that added to the caviar granules are 4.5 per cent by weight of sodium chloride, 0.2 per cent by weight of sodium glutamate, 0.1 per cent by weight

65

70

75

80

85

90

95

100

105

110

115

120

of sorbic acid, 0.2 per cent by weight of ascorbic acid, and 10 per cent by weight of corn oil, into which 5 per cent (with respect to the weight of oil) of dispersed natural caviar of sturgeon are preliminarily added to give caviar the characteristic taste and odour of natural caviar. The resultant product weighs 140 kg; the caviar contains the following components, in grams per kg of caviar:

	edible gelatin	50
	casein	120
	vegetable tannins	4-6
5	calcium alginate and ferric alginate	1-2
10	complex salts of ferric iron and vegetable tannins	0.005-0.01
15	corn oil	95
20	sodium chloride	45
25	sodium glutamate	2
	natural caviar of sturgeon	5
	sorbic acid	1
	ascorbic acid	2
	water	to make one kg.

The taste, colour and of the obtained granules resemble natural caviar of sturgeon. The granules remain solid at a temperature of 45°C for 45-50 minutes.

#### Example 34

Synthetic caviar imitating natural caviar of sturgeon is prepared by a procedure similar to that described in Example 33, except that after treatment of caviar granules with a solution of vegetable tannins, they are first treated with an aqueous solution of ferric lactate, and then with an aqueous solution of calcium acetate.

#### Example 35

Synthetic caviar resembling natural caviar of sturgeon is prepared by a procedure similar to that described in Example 33, except that an 0.2-0.5 per cent aqueous solution of low-ester value (ester value 50 per cent) pectin, having the pH 4.5-5.5, is used instead of the aqueous solution of sodium alginate.

#### Example 36

Prepared are 100 kg of a 10 per cent aqueous solution of food gelatin containing casein and edible vegetable oils (corn oil and cotton-seed oil). To that end, is prepared a stable emulsion on the basis of casein and edible vegetable oil by the procedure described in Example 9. Into said emulsion added are 10 kg of gelatin in the form of a 20-30 per cent aqueous solution.

The prepared 10 per cent aqueous solution of food gelatin containing casein and edible vegetable oils is passed through a fabric filter at a temperature of 50-60°C and, at the

same temperature, is introduced, in the form of droplets, into a mixture of equal parts of corn oil and cotton-seed oil. The lower layers of the oil mixture are cooled to the temperature of 4-7°C. Under these conditions the droplets of the starting solution form regular spheres of 2-4 mm in diameter. As they are cooled in the lower layers of the oil, gelatin is converted into gel.

The formed granules of gelatin, containing casein and edible vegetable oils, are washed with water at a temperature of 4-15°C and mixed with stirring for five minutes. The granules are then treated with an aqueous solution of vegetable tannins which is prepared by boiling 20-30 kg of finely cut coarse tea leaves in 300 litres of water for one hour, and cooled to 4-8°C before use. The granules are treated to a temperature of 4-15°C with stirring for 15-25 per minutes. As a result of this treatment, a dense slightly yellowish pellicle, consisting of the products of gel tanning, is formed on the granule surface.

On the termination of the tanning process, caviar granules are washed with water to remove unreacted tannins at a temperature of 4-8°C with stirring for 3-5 minutes. The granules are then treated with an 0.1 per cent aqueous solution of sodium alginate having a pH 4.5-5.5. The treatment is carried out with stirring at a temperature of 4-10°C for fifteen minutes. Then, the caviar granules are washed with water for three minutes at a temperature of 4-10°C and treated with an 0.1 per cent aqueous solution of ferric chloride at a temperature of 4-10°C with stirring for 3-5 minutes. As a result of the treatment with the solution of ferric chloride, the pellicle, consisting of the products of gel tanning with vegetable tannins, is coloured greyish-black due to the formation of complex salts of ferric iron with vegetable tannins. At the same time, another outer pellicle consisting of ferric alginate is formed on the surface of the granule. In order to increase the strength of the outer pellicle, caviar granules are treated with an 0.1 per cent aqueous solution of calcium acetate having a pH 4-5. The treatment is carried out at a temperature of 4-10°C with stirring for five minutes. As a result of this treatment calcium alginate, the component part of the outer pellicle, is formed.

Caviar granules coated with two pellicles, are washed with a 4-6 per cent aqueous solution of sodium chloride at a temperature of 4-15°C for 15 minutes (salting). Then, flavouring substances, preservatives, and corn oil are added to the caviar as described in Example 33.

#### Example 37

Synthetic caviar resembling natural caviar of sturgeon is prepared by a procedure similar

to that described in Example 36, except that after treatment with the aqueous solution of sodium alginate, and washing with water, the caviar granules, instead of being subsequently treated with aqueous solution of ferric chloride and calcium acetate, are treated with an aqueous solution containing 0.1 per cent by weight of ferric chloride, 0.07 per cent by weight of calcium chloride and 0.03 per cent by weight of aluminium chloride, and having a pH of 3.8—4.2.

#### Example 38

Synthetic caviar, with granules enclosed in two pellicles, resembling natural caviar of sturgeon is prepared by a procedure similar to Example 29, except that the culinary treatment is carried out as described in Example 17.

#### Example 39

Synthetic caviar with granules enclosed in two pellicles, resembling natural caviar of sturgeon, is prepared by a procedure similar to that described in Example 25, except that caviar granules are treated with a 0.2—1 per cent aqueous solution of aluminium-potassium sulphate or ammonium-aluminium sulphate at a pH 3.8—4.2, instead of the aqueous solution of calcium acetate.

The resultant caviar has granules, the outer pellicle of which, is formed by pectinates of aluminium and of ferric iron.

#### Example 40

Synthetic caviar, with granules enclosed in two pellicles, resembling natural caviar of sturgeon, is prepared by a procedure similar to that described in Example 5, except that after consecutive treatment of caviar granules with an aqueous solution of calcium chloride and an aqueous solution of a mixture of sodium alginate and low-ester value pectin, they are treated with an 0.1—0.2 per cent aqueous solution of ferric iron having a pH 4—5. As a result of this treatment, the pellicle consisting of the products of jell tanning with vegetable tannins is coloured greyish-black.

The obtained caviar is given the culinary treatment as described in Example 17.

The product resembles natural caviar of sturgeon with respect to its colour, taste and consistency. Caviar granules remain solid at a temperature of 45°C for thirty minutes.

#### Example 41

Synthetic caviar, with granules enclosed in two pellicles, resembling natural caviar of sturgeon, is prepared by a procedure similar to that described in Example 40, except that treatment of caviar granules with an aqueous solution of ferric chloride is followed by the treatment of caviar granules with an aqueous solution of a mixture of sodium alginate and

low-ester value pectin. The sequence in which these operations occur (as compared with Example 40) has no practical significance for the quality of the end product.

#### Example 42

Synthetic caviar, with granules enclosed in two pellicles, resembling natural caviar of sturgeon, is prepared by a procedure similar to that described in Example 1, except that after a consecutive treatment of caviar granules with an aqueous solution of sodium alginate and an aqueous solution of calcium acetate, they are treated with an 0.1—0.2 per cent aqueous solution of ferric chloride having a pH 4—5. The treatment is performed at a temperature of 4—15°C with stirring for 2—5 minutes. As a result of this treatment, the pellicle consisting of the products of jell tanning is coloured greyish-black.

The obtained caviar granules are given the culinary treatment as described in Example 17.

The product resembles natural caviar of sturgeon with respect to its colour, taste, and consistency. Caviar granules remain solid at a temperature of 35°C for one hour.

#### Example 43

Prepared are 100 kg of a 7 per cent greyish-black aqueous solution of food gelatin containing casein, corn oil, and cod-liver oil.

To that end, prepared first is greyish-black stable emulsion of corn oil and cod-liver oil in casein solution. The preparation of emulsion consists in the following. 5 kg of crushed coarse tea leaves in 50 litres of water are boiled for one hour to prepare 50 kg of solution of vegetable tannins. Said solution is cooled to room temperature and 0.2 kg of sodium hydroxide and 0.12 kg of ferric chloride are dissolved in it. The result is a black solution, having a pH 12. The black colour is due to the formation of complex salts of ferric iron with vegetable tannins. Next, 7.5 kg of casein are dissolved in the obtained black solution at a temperature of 50—60°C with stirring for two hours. The prepared 13 per cent black solution of casein, having a pH 6.2, is cooled to room temperature and 7.7 kg of an 0.5 per cent aqueous solution of sodium alginate are added. At the same time, there is prepared emulsion of 1 kg of 1 per cent aqueous solution of calcium acetate in a mixture of 6 kg of corn oil and 3 kg of cod-liver oil. The obtained emulsion is introduced, in a thin jet, into the coloured solution of casein and sodium alginate. During the process of emulsification, a protective coat of a gel of calcium alginate is formed on the surface of the oil phase droplets (the mixture of corn oil and cod-liver oil) to keep the droplets from coalescing and to prevent delamination of the emulsion.

To the obtained emulsion, added are 7 kg

65

70

75

80

85

90

95

100

105

110

115

120

of edible gelatin in the form of a 30 per cent aqueous solution, and the further process for preparing caviar is similar to that described in Example 1.

5 The resultant product is 125 kg of food caviar with granules enclosed in two pellicles that remain solid at a temperature of 35°C for 60 minutes. The aqueous gel of food gelatin, containing casein, corn oil, and cod-liver oil, is coloured greyish-black. The granule contents do not delaminate on storage in a refrigerator at a temperature of 4—8°C for 15 days.

10 The obtained product contains the following components, in grams per kg of caviar:

	edible gelatin	55	
	casein	70	
	corn oil	50	
	vegetable tannins	3—5	
20	calcium alginate	1.5—2	
	complex salts of ferric iron and vegetable tannins	0.001—0.005	
	water	to make one kg.	

#### 25 Example 44

Prepared are 100 kg of greyish-black 5 per cent aqueous solution of gelatin containing casein. To that end, 3.2 kg of green tea are boiled in 64 litres of water for 90 minutes, to prepare 64 kg of a solution of vegetable tannins. Said solution is cooled to room temperature and 0.26 kg of sodium hydroxide and 0.32 kg of ferric lactate are dissolved in it. The resultant greyish-black solution has a pH 12. The greyish-black colour with a brownish tint is due to the formation of complex salts of ferric iron with vegetable tannins. Next, 11 kg of casein are dissolved in the coloured alkaline solution, at a temperature of 50—60°C, with stirring for two hours. The greyish-black solution having a pH 6.2 is cooled to room temperature and 5 kg of food gelatin in the form of a 20 per cent aqueous solution are added to the casein solution. The further procedure is the same as described in Example 1.

50 Caviar granules, coated with two pellicles, are treated with a 5 per cent aqueous solution of sodium chloride at a temperature of 4—10°C with stirring for 3—5 minutes (salting). Then, to the granules added with stirring are 0.2 per cent by weight of sodium glutamate, 0.1 per cent by weight of sorbic acid, 0.1 per cent by weight of ascorbic acid, 0.05 per cent by weight of sodium inosinate, 3 per cent by weight of dry milk, 4 per cent by weight of corn oil, 4 per cent by weight of cotton-seed oil, 1 per cent by weight of cod-liver oil, 1.5 per cent by weight of herring juice, and 2 per cent by weight of hydrolyzate of soya-bean protein. The resultant product, weighing 110—125 per kg, contains the

following components, in grams per kg of caviar:

edible gelatin	40—45	65
casein	90—100	
vegetable tannins	4—5	
calcium alginate	1—1.5	
complex salts of ferric iron and vegetable tannins	0.005—0.01	70
sodium chloride	40	
herring juice	15	
sodium glutamate	2	
sodium inosinate	0.5	
corn oil	40	75
cotton-seed oil	40	
cod-liver oil	10	
dry milk	30	
hydrolyzate of soya-bean proteins	20	80
sorbic acid	1	
ascorbic acid	1	
water	to make one kg.	

The finished product resembles natural caviar of sturgeon with respect to its taste. The aqueous gel of gelatin containing casein is coloured greyish-black.

#### 25 Example 45

90 The starting greyish-black aqueous solution of food gelatin, containing casein, is prepared by a procedure similar to that described in Example 44. The obtained solution is passed through a fabric filter and introduced, in the form of droplets, at a temperature of 60°C, into a mixture of equal parts of corn oil and cotton-seed oil. The upper layers of the mixed oil are heated to the temperature of 40°C and the lower layers are cooled to the temperature of 3—10°C. Under these conditions the droplets of the starting solution are shaped into regular spheres, 2—4 mm in diameter. Since the viscosity of the oil in the upper layers is lowered owing to its heating, the spheres quickly pass them without coalescing, and slowly enter the lower cooled layers of the oil where the gelatin solution converts into gel.

95 The shaped and coloured granules are washed with water at a temperature of 4—10°C for five minutes, then treated with an aqueous solution of vegetable tannins, which is prepared by boiling 15—20 kg of green tea in 300 litres of water for 90 minutes and cooled to 4—8°C before use.

100 The granules are treated with the solution of tannins at a temperature of 4—8°C with stirring for 20—25 minutes. As a result of this treatment a dense, slightly yellowish pellicle is formed on the surface of the granule, the pellicle consisting of the products of jell tanning with the vegetable tannin solution.

110 On the termination of the tanning process, caviar granules are washed with water from

unreacted tannins at a temperature of 4—8°C for three to five minutes. The granules are then treated with an 0.2 per cent aqueous solution of ferric lactate at a temperature of 4—10°C with stirring for three to five minutes. As a result of the formation of complex salts of ferric iron and vegetable tannins adsorbed on the surface of the granules, the pellicle is coloured greyish-black. The granules of caviar are then washed with water at a temperature of 4—10°C for three minutes and treated with a 1 per cent aqueous solution of calcium acetate having a pH 4—5 at a temperature of 4—10°C with stirring for five minutes. The granules are then washed with water again at a temperature of 4—10°C and treated with an 0.1 per cent aqueous solution of sodium alginate, having a pH 4.5—5.5 at a temperature of 4—10°C with stirring for 15 minutes. As a result of this treatment, another, outer pellicle, consisting of calcium alginate and ferric alginate, is formed on the granule surface to give it high thermal stability. Caviar granules coated with two pellicles are washed with water at a temperature of 4—10°C for three minutes.

The finished product is food caviar, the granules of which are greyish-black both on the inside and outside the pellicle. The granules remain solid at a temperature of 40°C for 45 minutes.

#### Example 46

Synthetic caviar is prepared by a procedure similar to that described in Example 45, except that after treatment with the aqueous solution of sodium alginate, the caviar granules are treated with a 4—6 per cent aqueous solution of sodium chloride at a temperature of 4—15°C for 15 minutes (salting). To the granules there are added 0.2 per cent of sodium glutamate, 0.1 per cent by weight of sorbic acid, 0.1 per cent by weight of ascorbic acid, 10 per cent by weight of corn oil in which 0.5 per cent by weight of dispersed natural caviar of sturgeon is preliminarily added to give the product the specific taste and odour.

The finished product imitates natural caviar of sturgeon with respect to its taste and appearance. The granules are coloured greyish-black both on the outside and the inside. The granules remain solid at a temperature of 45°C for 40 minutes.

#### Example 47

Prepared are 100 kg of a 7 per cent greyish-black aqueous solution of food gelatin containing casein, corn oil, and cod-liver oil. The procedure for preparing said starting solution is described in Example 43. All other operations for preparing synthetic caviar are the same as described in Example 45.

The granules coated with two pellicles are kept for 5—10 minutes at a temperature of 8—12°C in a 4.5 per cent aqueous solution

of sodium chloride to salt the product. Then to the granules are added 0.3 per cent by weight of sodium glutamate, 0.15 per cent by weight of sorbic acid, 0.15 per cent by weight of ascorbic acid, 1 per cent by weight of corn oil, 0.004 per cent by weight of sodium inosinate, 0.003 per cent by weight of maltol, 0.003 per cent by weight of L-tryptophan, and 0.006 per cent by weight of alcoholic solution of flavouring additives having the following composition, in per cent by weight:

trimethylamine	4.9	
triethylamine	9.5	
pyridine	1.9	
piperidine	4.8	
n - propylamine	4.8	80
undecanone - 2	1.9	
diethylacetal of n - valeric aldehyde	4.8	
ethyl alcohol	67.4	

The finished product resembles natural caviar of sturgeon with respect to its taste, odour, and the appearance. The granules are coloured greyish-black, both on the inside and outside. The granules remain solid at a temperature of 40°C for 45 minutes. The granule contents do not delaminate on keeping the product in a refrigerator at a temperature of 4—8°C for two weeks.

#### Example 48

Prepared are 100 kg of an 8 per cent orange-red aqueous solution of food gelatin containing casein. To that end 15 kg of casein are dissolved in an 0.1N aqueous solution of sodium hydroxide at a temperature of 50—60°C with stirring for 1.5—2 hours. To the obtained caseins solution added are 15 kg of an edible annatto dye, viz., bixin (Hoffman-La-Roche, France) in the form a suspension in an 0.1N aqueous solution of sodium hydroxide. The obtained mixture is stirred thoroughly, and added to it are 8 kg of food gelatin in the form of a 20—30 per cent aqueous solution. Mixing is continued for another 30—60 minutes at a temperature of 50—60°C.

The obtained solution is introduced in the form of droplets into corn oil the temperature of which in its lower part is below the temperature at which the solution droplets congeal, namely, 4—7°C. Under these conditions the droplets of the starting solution assume the shape of regular spheres, 2—4 mm in diameter. As they are cooled in the lower layers of corn oil, gelatin solution is converted in to gel.

The shaped and coloured orange-red granules of gelatin gel, containing casein and annatto dye, are washed with water at a temperature of 4—15°C with stirring for 3—5 minutes. The granules are then separated from

water and treated with an aqueous solution of vegetable tannins which is prepared by boiling 15—20 kg of tea dust (wastes of tea manufacture resulting from the cutting, weighing, and packaging operations) in 300—400 litres of water for 60 minutes, and cooled before use to a temperature of 4—8°C. The granules are treated with this solution at a temperature of 4—8°C with stirring for 15—20 minutes.

As a result, a dense, slightly yellowish coat, consisting of the product of gel tanning, is formed on the jell granule surface.

On the termination of the tanning process the granules are washed with water from unreacted tannins at a temperature of 7—15°C for 5—7 minutes. The washed granules are treated with an 0.1 per cent aqueous solution of sodium alginate (or a 0.2 per cent aqueous solution of low-ester value beet pectin) having the pH 4—6, at a temperature of 4—15°C for 15 minutes. The granules are then separated from the solution of sodium alginate and treated with an 0.3—0.8 per cent aqueous solution of calcium acetate having the pH 4—5 for 2—5 minutes at a temperature of 4—15°C. As a result of this treatment of caviar granules with the aqueous solution of acid polysaccharide (sodium alginate) and calcium acetate, another, outer pellicle, consisting of calcium alginate, is formed on the surface of the granule to give thermal stability to caviar. Next, the granules are washed with water at a temperature of 4—15°C for 2—3 minutes. The resultant product weighs 115 kg. Food caviar contains the following components, in grams per kg of caviar:

edible gelatin	70
casein	130
vegetable tannins	4—5
annatto dye	0.14
calcium alginate	0.5—1
water	to make one kg.

The finished product resembles natural caviar of salmon with respect to its colour and the shape of granules. Caviar granules remain solid at a temperature of 35°C for 60 minutes.

#### Example 49

Synthetic caviar, prepared by a procedure described in Example 48, is given a culinary treatment consisting of adding 4—5 per cent by weight of sodium chloride, 0.2 per cent by weight of sodium glutamate, 0.15 per cent by weight of sorbic acid, 0.15 per cent by weight of ascorbic acid, 10 per cent by weight of corn oil into which 1—2 per cent by weight of dispersed natural caviar of salmon are preliminarily added to give the product the specific taste and odour of natural caviar. The resultant product weighs 130—132 kg.

The obtained caviar contains the following components in grams per kg of caviar:

edible gelatin	61—62	65
casein	115	
vegetable tannins	4—5	
calcium alginate	0.5—1	
annatto dye	0.12	
sodium chloride	40—50	70
sodium glutamate	2	
natural caviar of salmon	10—20	
corn oil	100	
sorbic acid	1.5	
ascorbic acid	1.5	75
water	to make one kg.	

The finished product resembles natural caviar of salmon with respect to its colour, taste, and odour. The granules remain solid at a temperature of 35°C for 60 minutes.

#### Example 50

100 kg of a 4 per cent orange-red aqueous solution of food gelatin containing casein are prepared. To that end, 15 kg of casein are dissolved in 0.1N aqueous solution of sodium hydroxide at a temperature of 50—60°C with stirring for 1.5—2 hours. To the obtained casein solution added are 3 g of an edible annatto dye, viz., bixin (Hoffman-La-Roche, France) in the form of a 0.05 per cent solution in corn oil. The obtained mixture is stirred thoroughly and are added 5 kg of food gelatin in the form of a 20—30 per cent aqueous solution. Stirring is continued for another 15 minutes at a temperature of 50—60°C. The further procedure for preparing caviar granules is the same as described in Example 48. The finished product weighs 100 kg.

#### Example 51

Synthetic caviar with granules coated in two pellicles resembling natural caviar of salmon with respect to its colour and granule shapes, is prepared as described in Example 48, except that 22.5 g of eno dye are used instead of the 15 g of annatto dye. The resultant product weighs 113 kg.

#### Example 52

Synthetic caviar prepared in Example 51, is given the organoleptic properties imitating those inherent in natural caviar of salmon, and also protected from bacterial contamination by the following culinary treatment.

Caviar granules coated with two pellicles are kept for 5 minutes in a 5 per cent aqueous solution of sodium chloride at a temperature of 5—10°C (salting). Then, to the granules are added 0.2 per cent by weight of sodium glutamate, 0.15 per cent by weight of sorbic acid, 0.15 per cent by weight of ascorbic acid, 10 per cent by weight of corn oil into which 1—2 per cent by weight of dispersed caviar of

- salmon are dispersed to give the product the specific taste and odour of natural salmon caviar.
- The finished product resembles natural caviar of salmon with respect to its colour, taste, and odour. The granules of caviar remain solid at a temperature of 45°C for 40 minutes.
- Our copending application no. 12831/75 (Serial No. 1474666) describes and claims synthetic caviar comprising granules of an aqueous gel of edible gelatin and containing edible protein, each granule being enclosed within two pellicles, an inner pellicle consisting of the product of tanning said gel with a vegetable tannin and also a complex ferric salt of a vegetable tannin, and an outer pellicle containing a ferric salt of an acid polysaccharide.
- WHAT WE CLAIM IS:—**
1. Synthetic caviar comprising granules of an aqueous gel of edible gelatin containing edible proteins and enclosed in two pellicles namely an inner pellicle consisting of the products of tanning said gel with a vegetable tannin, and an outer pellicle containing a calcium and/or aluminium salt of an acid polysaccharide.
  2. Synthetic caviar as claimed in Claim 1, in which the acid polysaccharide is a water-soluble alginate or a pectin having an ester value of not higher than 50 per cent.
  3. Synthetic caviar as claimed in Claim 1 or 2, containing the following components, in grams per kg of caviar:
- |  |                 |
|--|-----------------|
| edible gelatin                                       | 40—80           |
| edible proteins                                      | 35—140          |
| vegetable tannin                                     | 2—6             |
| calcium and/or aluminium salt of acid polysaccharide | 0.1—2           |
| water  | to make one kg. |
4. Synthetic caviar as claimed in Claim 1 or 2 or 3, in which the aqueous gel of edible gelatin contains also lipids at a concentration of 3—70 g per kg of caviar.
  5. Synthetic caviar as claimed in any preceding claim, in which the aqueous gel of edible gelatin contains also a carbohydrate at a concentration of 3—40 g per kg of caviar.
  6. Synthetic caviar as claimed in any preceding Claim, in which the aqueous gel of edible gelatin contains also a vitamin at a concentration of 0.001—0.02 g per kg of caviar.
  7. Synthetic caviar as claimed in any preceding Claim, in which the aqueous gel of edible gelatin contains also a complex salt of ferric iron and vegetable tannins each in a concentration of 0.001—0.01 g per kg of caviar.
  8. Synthetic caviar as claimed in any preceding Claim, in which the inner pellicle, consisting of the products of tanning the gel with a vegetable tannin, contains a complex salt of ferric iron and vegetable tannin, each at a concentration of 0.001—0.01 g per kg of caviar, and the outer pellicle which contains a calcium and/or aluminium salt of an acid polysaccharide, also contains a ferric salt of an acid polysaccharide in a concentration of 0.1—2 g per kg of caviar.
  9. Synthetic caviar as claimed in any one of Claims 1 to 7, in which the aqueous gel of edible gelatin and the inner pellicle which consists of the products of tanning the gel with a vegetable tannin, contain also a salt of ferric iron and vegetable tannins, each at a concentration of 0.001—0.1 g per kg of caviar, and the outer pellicle which contains a calcium and/or aluminium salt of an acid polysaccharide, contains also a ferric salt of an acid polysaccharide, at a concentration of 0.1—2 g per kg of caviar.
  10. Synthetic caviar as claimed in any preceding claim in which the aqueous gel of edible gelatin contains also an edible emu or annatto dye at a concentration of 0.03—0.2 g per kg of caviar.
  11. Synthetic caviar as claimed in any preceding claim, in which the granular mass of caviar contains vegetable oil, sodium chloride and flavouring substances in the following quantities, in grams per kg of caviar:
- |                       |        |
|-----------------------|--------|
| vegetable oil         | 10—100 |
| sodium chloride       | 30—50  |
| flavouring substances | 3—30   |
12. Synthetic caviar as claimed in Claim 11, in which the granular mass of caviar contains also additional lipid material in the quantity of 20—120 g per kg of caviar.
  13. Synthetic caviar as claimed in Claims 11 or 12, in which the granular mass of caviar contains also an amino acid, a vitamin and a preservative, taken separately or in various combinations, in the quantity of 3—30 g per kg of caviar.
  14. A method for preparing synthetic caviar, comprising introducing a 4—10 per cent aqueous solution of edible gelatin containing edible protein, in the form of droplets, into an edible oil the temperature of which, at least in its lower layers, is below the temperature at which the droplets of said solution congeal, thus forming granules of gelatin gel which contain edible protein, washing the granules with water to remove edible oil and treating the washed granules with an aqueous solution of a vegetable tannin, washing the tanned granules with water to remove unreacted vegetable tannin, and treating the washed granules with an aqueous solution of an acid polysaccharide and with a solution of an edible calcium and/or aluminium salt

thereby to form a calcium and/or aluminium salt of the acid polysaccharide.

15. A method as claimed in Claim 14, in which the aqueous solution of acid polysaccharide is a soluble alginate or pectin having an ester value of not higher than 50 per cent, in the form of aqueous solution thereof having a concentration of 0.01—0.5 per cent and a pH from 3 to 7.

10 16. A method as claimed in Claim 14, in which the 4—10 per cent aqueous solution of edible gelatin and edible protein, also contains a lipid, a carbohydrate, and a vitamin, taken either separately or in various combinations.

15 17. A method as claimed in Claim 14, in which, after having been washed with water to remove unreacted vegetable tannin, the granules are treated first with an aqueous solution of an acid polysaccharide and then 20 with an aqueous solution of an edible calcium and/or aluminium salt.

18. A method as claimed in Claim 14, in which after having been washed with water to remove unreacted vegetable tannin, the 25 granules are treated first with an aqueous solution of an edible calcium and/or aluminium salt and then with an aqueous solution of an acid polysaccharide.

19. A method as claimed in Claims 14, 15 30 or 16, in which the 4—10 per cent aqueous solution of edible gelatin also contains an edible ferric salt and a vegetable tannin.

20. A method as claimed in Claims 14, 15 35 or 16, in which the 4—10 per cent aqueous solution of edible gelatin also contains an edible emu or annatto dye.

21. A method as claimed in any one of Claims 14 to 19, in which the prepared caviar 40 granules are treated with an aqueous solution of an edible ferric salt.

22. A method as claimed in Claim 21, in which caviar granules are treated with an aqueous solution of an edible ferric salt in combination with an aqueous solution of an 45 edible calcium and/or aluminium salt.

23. A method as claimed in Claim 21, in which caviar granules are treated with an

squeous solution of an edible ferric salt following their treatment with an aqueous solution of an acid polysaccharide, and then the caviar granules are treated with aqueous solution of an edible calcium and/or aluminium salt.

24. A method as claimed in Claim 21, in which caviar granules are treated with an aqueous solution of an edible ferric salt following after their washing to remove unreacted vegetable tannin, and then the caviar granules are treated with an aqueous solution of an acid polysaccharide and an aqueous solution of an edible calcium and/or aluminium salt.

25. A method as claimed in any one of Claims 14 to 24, in which the obtained caviar granules are given a culinary treatment comprising salting the caviar granules with sodium chloride and adding vegetable oil and flavouring substances.

26. A method as claimed in Claim 25, in which the culinary treatment includes adding to the granules a lipid, an amino acid, a vitamin, and a preservative, taken separately or in various combinations.

27. Synthetic caviar as claimed in Claims 1 to 13, substantially as hereinbefore described.

28. A method for preparing synthetic caviar, as claimed in Claims 14 to 26, substantially as hereinbefore described.

29. Synthetic caviar and a method of preparing same according to any one of Examples 1 to 52.

50

55

60

65

70

75

80

FITZPATRICKS,  
Chartered Patent Agents,  
14—18 Cadogan Street,  
Glasgow G2 6QW.  
—and—  
Warwick House,  
Warwick Court,  
London WC1R 5DJ.

Reference has been directed in pursuance of section 9, subsection (1) of the Patents Act 1949, to patent No's. 1300721 and 1167507.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1977  
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from  
which copies may be obtained.